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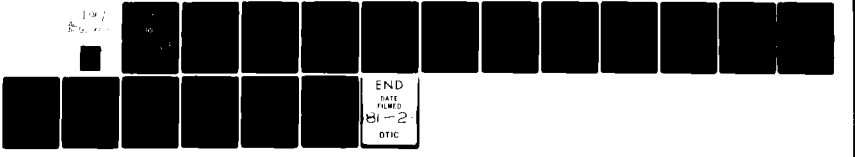

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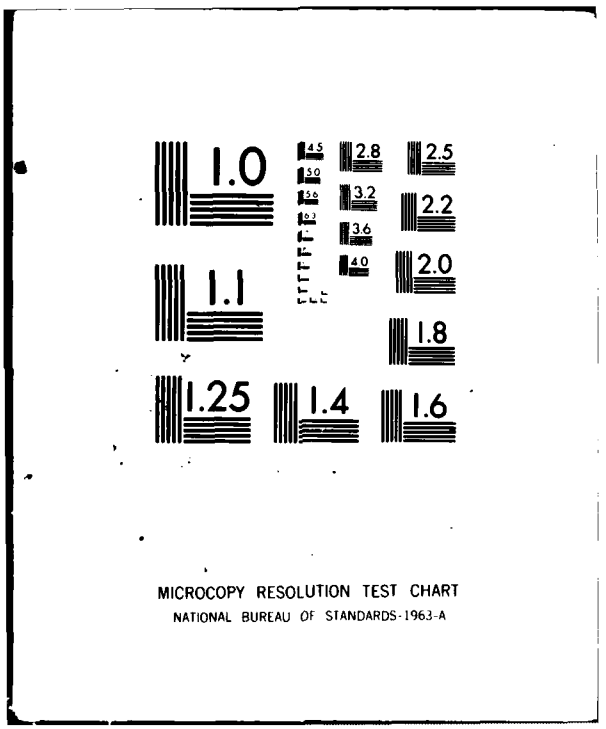
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3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): Chemiluminescence of Dioxetanone Investigated by Self Consistent Field Theory	5. TYPE OF REPORT & PERIOD COVERED: Technical
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Steven P. Schmidt, Mark A. Vincent, Clifford E. Dykstra, Gary B. Schuster	8. CONTRACT OR GRANT NUMBER(s): N0014-76-0745 ✓
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry ✓ University of Illinois Urbana, IL 61801	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR-051-616
11. CONTROLLING OFFICE NAME AND ADDRESS: Chemistry Program, Materials Science Division, Office of Naval Research, 800 N. Quincy Street Arlington, VA 22217	12. REPORT DATE: November 14, 1980
	13. NUMBER OF PAGES: 18
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
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peroxides
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SCF calculations using a 4-31G basis set were performed on dioxetanone. The results indicate that the four ring atoms of this peroxide are essentially coplanar. Also, stretching of the oxygen-oxygen bond does not lead to a concomitant increase in the carbon-carbon bond distance. This finding is taken to indicate that the thermal reaction of dioxetanone proceeds through a biradical. A rationalization of the very different yields of excited state products from dioxetane and dioxetanone is based upon this conclusion. The (cont.)

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properties of the radical anion obtained by adding an electron to the 16a' orbital were probed computationally. It was found that increasing the oxygen-oxygen bond distance of the anion results in a remarkable decrease in energy. This finding is taken as support of the details of the chemically initiated electron-exchange luminescence (CIEEL) path suggested to be responsible for the majority of the chemiluminescence for dioxetanones.

(15) N0014-76-C-0745

OFFICE OF NAVAL RESEARCH

Contract N0014-76-C-0745

Task No. NR-501-616

(9) TECHNICAL REPORT NO. N0014-76-C-0745-29

(6) Chemiluminescence of Dioxetanone Investigated by Self Consistent Field Theory.

by

Steven P. Schmidt, Mark A. Vincent, Clifford E. Dykstra, Gary B. Schuster

Prepared for Publication

in

(11) 14 Nov 80 (12) 7

Journal of the American Chemical Society

School of Chemical Sciences

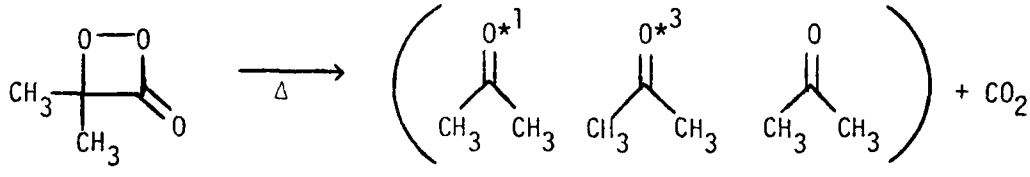
University of Illinois

Urbana, Illinois 61801

October 31, 1980

Sir:

The unusual facility of the four-membered ring peroxides to generate electronically excited states by thermolysis has focused attention on their chemical behavior.[1] In recent reports we have described our findings on the chemical behavior of dimethyldioxetanone (1).[2,3,4,5] In particular we find that thermolysis of dioxetanone 1 in any one of a number of non-polar solvents at 30°C gives both excited singlet and triplet acetone in yields of 0.1% and 1.5% respectively; eq. 1.[3] Also, we find that dioxetanone 1 is subject to catalytic decomposition by electron donors (ACT), and excited state generation by the path we have designated chemically initiated electron exchange luminescence (CIEEL);[4,6] eq. 2.



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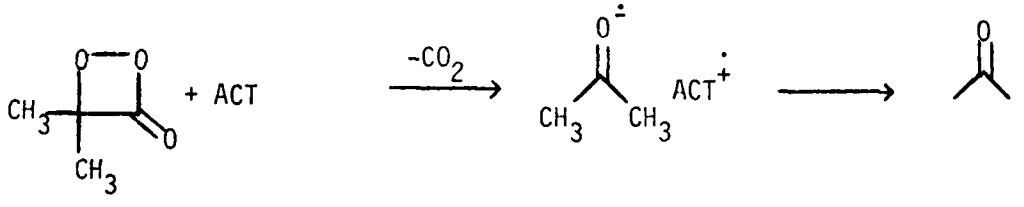


(2)

Tetramethyldioxetane (2) also generates electronically excited acetone upon thermolysis.[7] However, in contrast to dioxetanone 1 it does not react readily with electron donors, and the yield of excited acetone from 2 is nearly 20 times greater than from 1 despite the fact that the dioxetanone rearrangement is more exothermic by ca. 20 kcal/mole.[8] Herein we report the results of theoretical calculations on the parent unsubstituted dioxetanone. These calculations offer considerable insight into the structure and reactivity of this molecule, and provide a basis for understanding the different properties of peroxides 1 and 2.

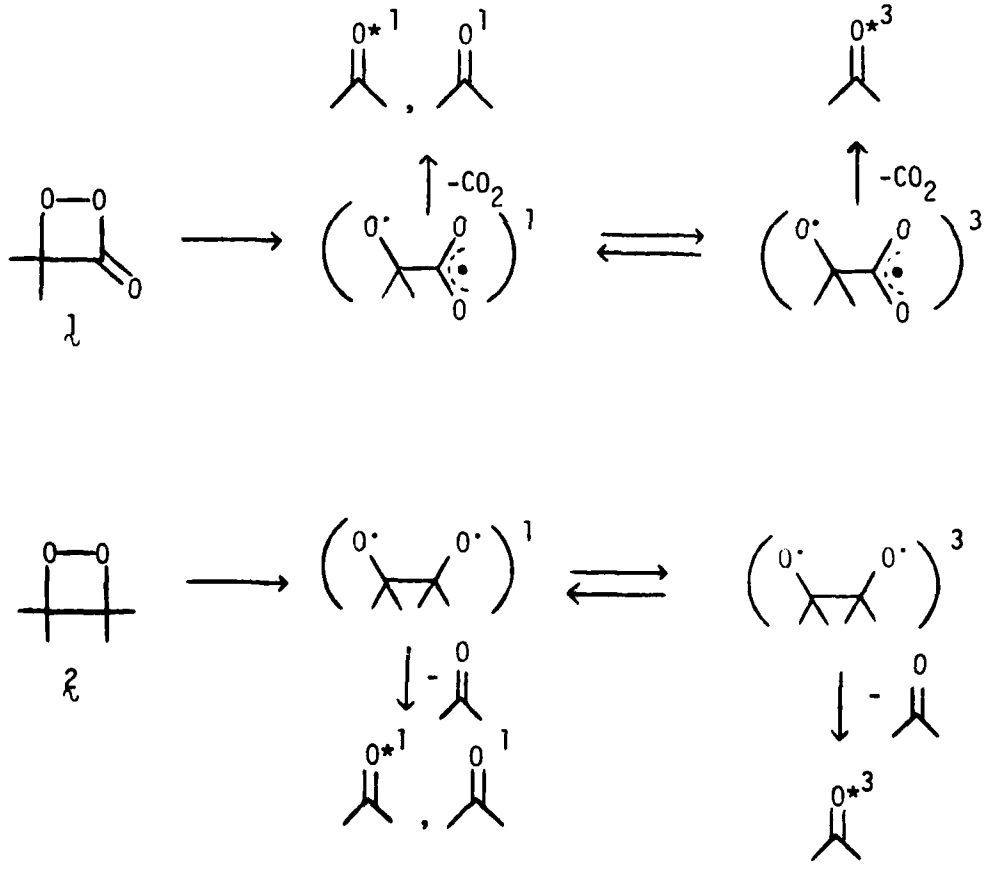
SCF calculations were performed on dioxetanone using a 4-31G basis set[9] of contracted Gaussian functions. The equilibrium structure, shown in Figure 1, was determined using the gradient procedure of Pulay,[10] and by point-by-point serches. The energetics of stretching the oxygen-oxygen bond was investigated by fixing its length and then re-optimizing the two C-O-O ring angles, constraning the ring to be planar in these calculations. The effect of increasing the oxygen-oxygen bond length on the energy of the molecule is given in Table 1. Orbital energies at these distorted structures are given in Table 2, and plots of selected orbitals are given in Figure 2.[11] SCF energies of the $^2A'$ anion state, formed by adding an electron to the 16a' orbital, were calculated at these optimized structures.

The equilibrium ground-state structure of dioxetanone that is predicted by these calculations has two noteworthy aspects. The oxygen-oxygen bond length is somewhat longer than that determined by X-ray crystallography for adamantylideneadamantane-1,2-dioxetane (3) by Wynberg and coworkers.[12] However, the most surprising feature of the predicted structure of dioxetanone is that the atoms of the four membered ring are found to be essentially coplanar. This finding is in contrast to the structure of dioxetane 3 in which one oxygen atom of the peroxide is lifted ca. 21° from the plane defined by the remaining ring atoms.

Of significance to the understanding of the thermal chemistry of dioxetanone is the prediction that stretching the oxygen-oxygen bond does not cause a concomitant increase in the length of the ring carbon-carbon bond, Table 1. Although we have not carried the calculations all the way through to the transition state, progress along the reaction coordinate is significant since the energy increase obtained in a substantial fraction of the experimentally determined activation

enthalpy for dioxetanone 1. The implication of these findings is that the thermolysis of dioxetanone may proceed through the biradical state formed by crossing of the 14a' and 16a' orbitals as a result of cleavage of the oxygen-oxygen bond. A similar conclusion was reached by Goddard and Harding[13] for dioxetane using GVB calculations. This conclusion is supported by extensive experimental evidence.[14]

These findings suggest an explanation for the difference in excited state yields obtained from thermolysis of dioxetanone 1 and dioxetane 2. Cleavage of the oxygen-oxygen bond in both cases leads to a biradical presumably initially in a singlet state. Intersystem crossing to the triplet biradical is therefore in competition with cleavage of the ring carbon-carbon bond; Scheme 1.



For the case of dioxetanone the loss of CO_2 competes with intersystem crossing; for dioxetane it is the loss of a simple carbonyl compound that is in competition with intersystem crossing. The former is more exothermic and, therefore, is probably more rapid, giving the biradical less opportunity to cross to the triplet manifold. Consistent with this postulate is the experimental observation that the yield of excited singlet acetone from thermolysis of 1 and 2 is quite similar, but the yield of triplet acetone from 1 is considerable reduced from that of 2.[3]

Our formulation of the CIEEL mechanism has as a key tenet the activated transfer of an electron from an electron donor to the peroxide. We postulate further that the oxygen-oxygen bond of the peroxide cleaves either simultaneously with the transfer of the electron or very rapidly following its arrival. Several of the results of the calculation bear on this mechanism. First, transfer of an electron from an activator (perylene, for example) to dimethyldioxetanone is estimated from electrochemical data to be endothermic at the equilibrium ground state geometry.[15] Indeed, we have measured the activation energy for this process and find it to be 16 kcal/mole. The calculations show that stretching the oxygen-oxygen bond of dioxetanone results in a large decrease in the energy of the unoccupied 16a' orbital (Table 2), thereby facilitating the electron transfer. Thus, as we have previously suggested, the activating process for the electron transfer in the CIEEL mechanism is most likely stretching of the oxygen-oxygen bond.

The second result of the calculation that aids in the description of the CIEEL mechanism concerns the energy of the radical anion obtained by placing an electron in the 16a' orbital. This orbital is antibonding between the peroxide oxygens, Figure 2d. Table 3 lists the energy of the anion at various oxygen-oxygen bond distances. The striking result is that on increasing this

bond distance 0.2 Å from its equilibrium value the energy of the anion drops by ca. 52 kcal/mole. We take this result to indicate that the oxygen-oxygen bond of the radical anion of dioxetanone is dissociative and that irreversible cleavage follows immediately the receipt of the electron. This conclusion is entirely consistent with our experimental observations on the dioxetanone system.

In sum, these calculations provide new insight into the detailed chemistry of dioxetanone, though highly quantitative predictions will require more extensive calculations. They substantiate a reasonable rationalization of the different yields observed from dioxetanone 1 and dioxetane 2. And they provide some confirmation of the major postulates of the CIEEL mechanism.

Acknowledgment:

We thank Peter Dardi and Suketu Gandhi for assistance in generating the MO plots. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the Office of Naval Research and the National Science Foundation.

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Table 1. Dioxetanone Structures and Relative Energies.

R_{O-O}(Å)	R_{C-C}(Å)	∠COO[a]	∠COO[b]	E(a.u.)	ΔE(kcal)
1.503	1.502	89.5	90.5	-300.8921	0.0
1.525	1.502	89.0	90.0	-300.8919	0.2
1.55	1.502	88.5	89.5	-300.8910	0.7
1.60	1.501	87.7	88.4	-300.8877	2.8
1.70	1.501	85.5	86.5	-300.8765	9.8

[a]The methylene carbon atom is referred to.

[b]The carbonyl carbon atom is referred to.

Table 2. Dioxetanone Orbital Energies.[a]

		R_{00}				
		1.503	1.525	1.55	1.60	1.70
Virtual	18a'	0.237	0.236	0.234	0.233	0.231
	17a'	0.214	0.214	0.214	0.214	0.214
	16a'	0.138	0.127	0.114	0.090	0.046
	5a"	0.123	0.123	0.124	0.124	0.125
Occupied	4a"	-0.483	-0.486	-0.489	-0.493	-0.501
	15a'	-0.492	-0.492	-0.492	-0.491	-0.490
	14a'	-0.577	-.0573	-0.568	-0.558	-0.537
	3a"	-0.586	-0.585	-0.583	-0.580	-0.575
	13a'	-0.601	-0.603	-0.605	-0.609	-0.617
	2a"	-0.628	-0.628	-0.628	-0.629	-0.631
	12a'	-0.724	-0.723	-0.722	-0.720	-0.717
	11a'	-0.745	-0.744	-0.742	-0.738	-0.733
	1a"	-0.762	-0.760	-0.758	-0.756	-0.751

[a]Orbital energies were evaluated at the structures in Table 1 and are given in a.u.

Table 3. Anion Energies.[a]

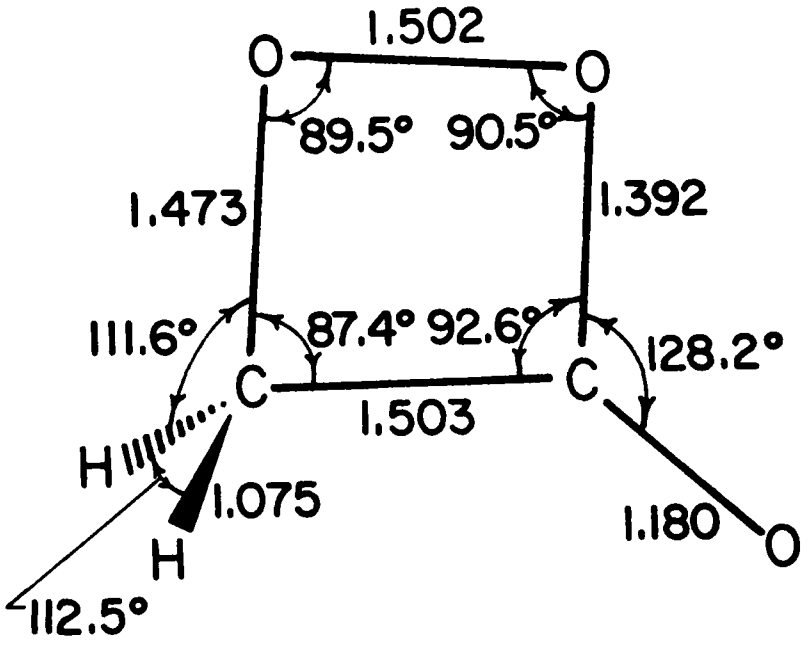
R_{O-O}(Å)	E(a.u.)	ΔE(kcal)
1.503	-300.8284	0.0
1.525	-300.8419	-8.5
1.55	-300.8555	-17.0
1.60	-300.8780	-31.2
1.70	-300.9111	-51.9

[a]Structures used were those in Table 1.

Figure Captions

Figure 1. Optimized equilibrium structure of dioxetanone.

Figure 2. Molecular orbital contour plots[11] of the occupied or internal orbitals, (a) 13a', (b) 14a', and (c) 15a', and the virtual or external orbital (d) 16a'.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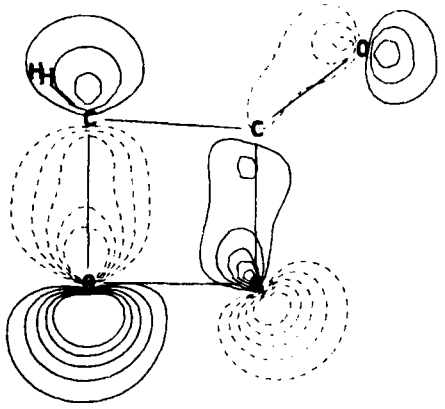

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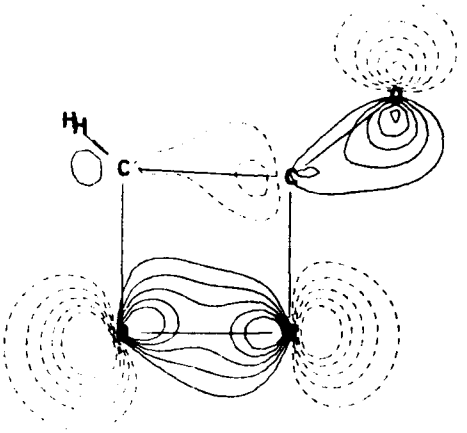

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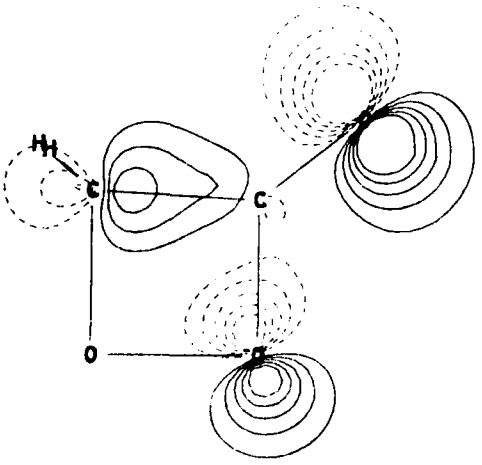

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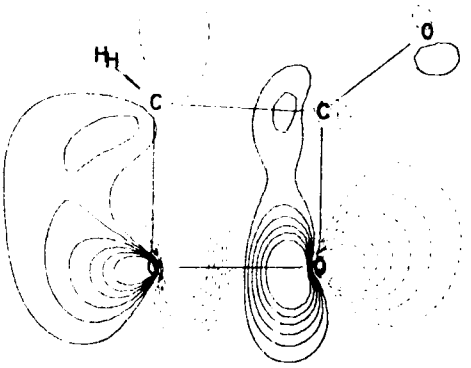

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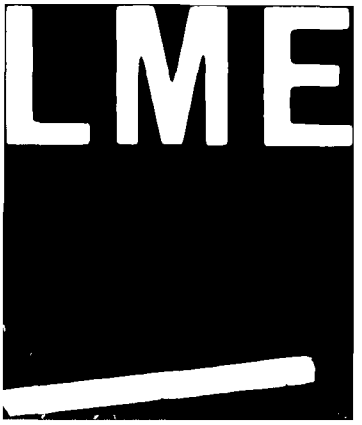
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